

Deuterium and Hydrogen Electrode Characteristics of Lithia-Silica Glasses

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The pH and pD responses of a series of lithia-silica glasses have been investigated and compared with the hygroscopicity, deuterioscopicity, and chemical durability of the glasses in aqueous and deuterium oxide buffers. The curves for pH and pD response as a function of composition pass through an optimum electrode response that is limited on the low percentage of silica end by poor chemical durability and a strong tendency to devitrify upon reheating the glasses for the purpose of blowing the electrodes. The optimum also falls off on the high-silica end where opalescence appears and the hygro- and deuterioscopicities decrease.

The pH and pD response, hygroscopicity, and deuterioscopicity, as well as the chemical durability in aqueous and deuterium oxide solutions, appear to reflect some of the critical features of the $\text{Li}_2\text{O}-\text{SiO}_2$ phase equilibrium diagram, with the optimum electrode response occurring in the composition range in which tridymite is the primary phase.

Indices of refraction and expansion data for these $\text{Li}_2\text{O}-\text{SiO}_2$ glasses exhibit breaks at the same compositions indicated by the physicochemical properties.

1. Introduction

Electrodes prepared from silicate glasses whose compositions include substantial percentages of Li_2O have become commercially accepted in recent years because of their favorable voltage response to hydrogen-ion activity in aqueous solutions over an extended range of pH, alkaline salt concentrations, and temperature [1 to 4].¹ Considerable confusion, however, still prevails in the readily available literature concerning the use of Li_2O in electrode glasses [5 to 10]. The present investigation was undertaken to ascertain whether a series of $\text{Li}_2\text{O}-\text{SiO}_2$ glasses exhibited any unusual features in regard to the normal dependence of pH response upon the properties of suitable chemical durability and adequate hygroscopicity [11 to 13]. In addition, a study of the deuterioscopicity,² chemical durability to deuterium oxide solutions, and the electrode response (pD) of these $\text{Li}_2\text{O}-\text{SiO}_2$ glasses to deuterium-ion activity were undertaken.

The experimental procedures employed for determining the deuterioscopicity, pD response, and the chemical durability to deuterium buffers of this series of glasses were similar to the procedures reported in previous investigations on other glass series for hygroscopicity, pH response, and chemical durability to aqueous solutions [11 to 13].

2. Hygroscopicity and Deuterioscopicity

The hygroscopicity and deuterioscopicity values listed in table 1 and plotted in figure 1 were obtained on two series of $\text{Li}_2\text{O}-\text{SiO}_2$ glasses. One of these series (○) was that studied for density and reported by Young and his colleagues [14]. Their glasses had been analyzed and carefully annealed by a cooling

schedule designed to place each member of the series in a comparable condition. The hygroscopicity and deuterioscopicity composition curves for these glasses demonstrated abrupt changes at the same compositions indicated by the density composition curve [14] and by other hygroscopicity composition data obtained by a different procedure and reported in an earlier publication [15]. Data for index of refraction³ and expansion⁴ obtained on this same series of glasses are presented in table 2 and figure 2 because they emphasize the same composition features shown by the hygroscopicity and deuterioscopicity curves.

For all properties studied on this analyzed and carefully annealed series of glasses, including the amounts of H_2O and D_2O retained upon reheating at 110°C after the completion of the hygroscopicity and deuterioscopicity experiments, distinct changes in the slopes are indicated near 82 and 77 percent of SiO_2 . The break at the higher percentage of SiO_2 corresponds very closely to the eutectic composition between the compounds $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ and tridymite, while the other is approximately 2 percent lower in SiO_2 than the transition point reported between $\text{Li}_2\text{O} \cdot \text{SiO}_2$ and $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ [19].

The compositions for the members of the new series of $\text{Li}_2\text{O}-\text{SiO}_2$ glasses whose hygroscopicity and deuterioscopicity are plotted (+) in figure 1 were calculated from the batch compositions. No definite schedule had been observed in cooling through the annealing range.

The exaggerated difference in the two series of glasses can probably be ascribed to the extent of the departure from randomness of the silica network. This is strongly supported by the fact that the lithia-silica glasses show a marked tendency to crystallize in the composition ranges in which $\text{Li}_2\text{O} \cdot \text{SiO}_2$ and SiO_2 are the primary phases.

³ These index of refraction values were obtained by C. A. Faick, using an immersion method [16, 17].

⁴ These expansion data were taken by L. H. Maxwell, using the Saunders' modified Fizeau interferometric procedure [18].

¹ Figures in brackets indicate the literature references at the end of this paper.
² "Deuterioscopicity" is the expression applied to D_2O sorption corresponding to the term "hygroscopicity."

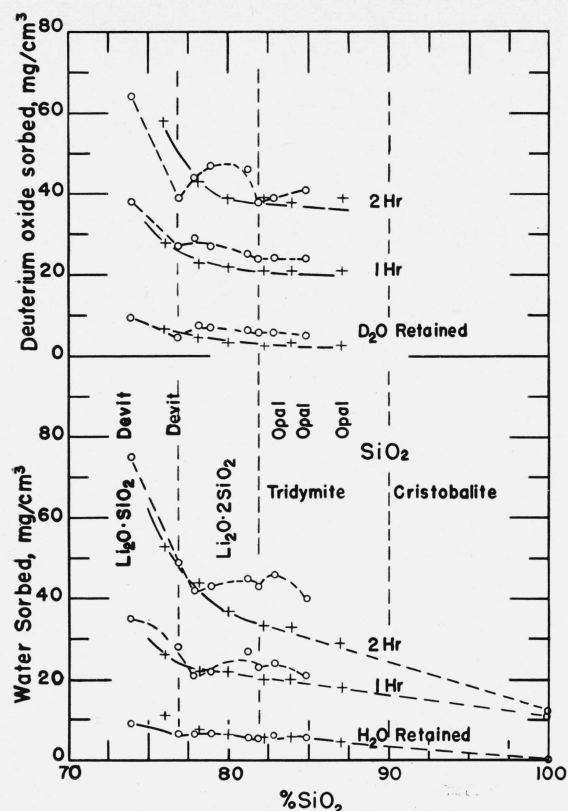


FIGURE 1. Hygroscopicity and deuteroscopicity of two series of $\text{Li}_2\text{O-SiO}_2$ glasses.

(o), glasses annealed and analyzed [14]; (+), glasses having no definite annealing schedule and whose compositions were calculated from batch compositions.

TABLE 1. Hygroscopicity and deuteroscopicity of two series of $\text{Li}_2\text{O-SiO}_2$ glasses

A. Annealed and analyzed glasses of Young, Glaze, Faick, and Finn [14]							
Glasses		Water (H_2O)			Deuterium oxide (D_2O)		
Li_2O	SiO_2	Sorbed 1 hr	Sorbed 2 hr	Retained	Sorbed 1 hr	Sorbed 2 hr	Retained
%	%	mg/cm ³	mg/cm ³	mg/cm ³	mg/cm ³	mg/cm ³	mg/cm ³
26.13	73.87	35	75	8.8	38	64	9.7
23.18	76.82	27	49	6.4	27	39	4.6
22.20	77.80	21	42	6.5	29	44	7.7
21.09	78.91	22	43	6.7	27	47	7.0
18.73	81.27	27	45	5.5	25	46	6.1
18.11	81.89	23	43	5.2	24	38	5.9
17.05	82.95	24	46	6.0	24	39	5.9
15.12	84.88	21	40	5.6	24	41	5.0
Fused SiO_2		11	12	0	----	----	----
B. Glasses whose compositions were calculated from the batch composition							
23.9	76.1	26	53	11.0	28	57	6.9
21.8	78.2	22	44	7.4	23	43	4.3
20.0	80.0	22	37	6.3	22	39	3.4
17.8	82.2	20	33	5.4	21	39	2.5
16.1	83.9	20	33	5.9	21	38	3.1
12.9	87.1	19	28	4.2	21	39	2.3
Corning 015 ^a		104	168	-----	----	----	----

^a A commercial electrode glass included for comparison.

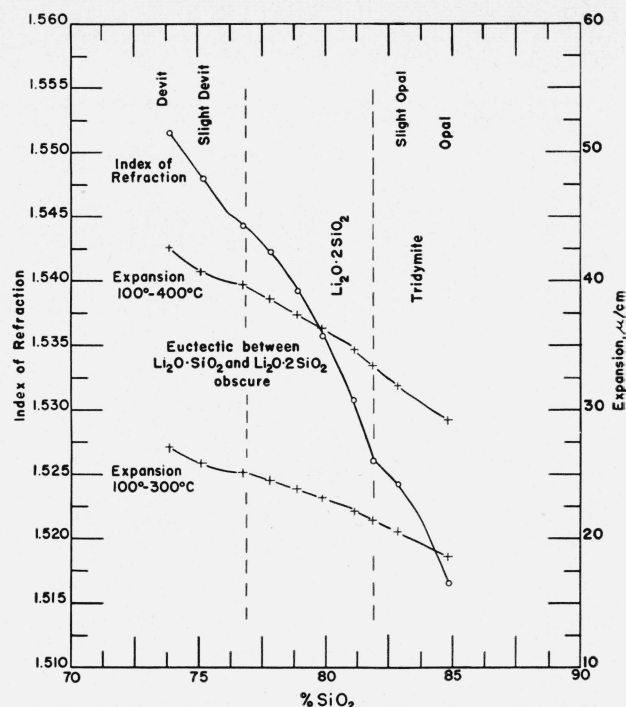


FIGURE 2. Indices of refraction and expansion characteristics of a series of $\text{Li}_2\text{O-SiO}_2$ glasses.

TABLE 2. Index of refraction ($\text{Na } \lambda=5889$) and expansion characteristics of a series of $\text{Li}_2\text{O-SiO}_2$ glasses

Glasses		Expansion				Critical temperature	Softening temperature	Index of refraction
Li_2O	SiO_2	100° to 300° C	100° to 400° C	100° CT ^a	100° ST ^b			
%	%	μ/cm	μ/cm	μ/cm	μ/cm	°C	°C	
26.13	73.87	27.1	42.6	50.7	60.7	445	475	1.5515
24.81	75.19	25.9	40.7	48.0	58.0	445	475	1.5480
23.18	76.82	25.1	39.7	48.7	54.7	450	475	1.5443
22.20	77.80	24.5	38.6	48.5	56.0	460	485	1.5423
21.09	78.91	23.8	37.3	46.2	56.7	460	490	1.5392
20.06	79.94	23.1	36.3	45.0	56.0	460	490	1.5357
18.73	81.27	22.1	34.7	44.1	46.6	465	480	1.5307
18.11	81.89	21.4	33.5	42.8	49.8	465	495	1.5260
17.05	82.95	20.5	31.8	39.7	47.7	455	480	1.5242
15.12	84.88	18.6	29.2	36.7	43.2	460	490	1.5165
Fused SiO_2		-----	-----	-----	-----	-----	-----	1.4567

^a CT, critical temperature.

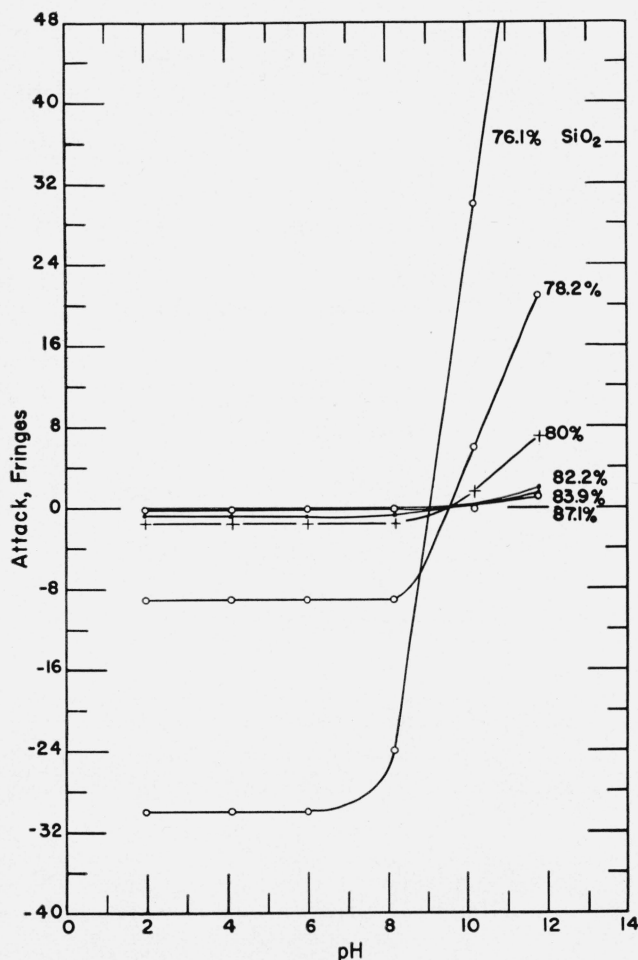
^b ST, softening temperature.

3. Chemical Durability

The chemical durabilities of the $\text{Li}_2\text{O-SiO}_2$ glasses over an extended pH range are listed in table 3 and plotted in figure 3. These durability data, obtained by an interferometer procedure [20, 21], illustrate the familiar swelling in the acid range (represented as negative attack in the figure), and the usual solution of the glass in the alkaline buffers. These durability features are characteristic of many silicate glasses exposed to the Britton-Robinson universal buffer mixtures at 80° C [11 to 13].

TABLE 3. Chemical durability and pH response of $\text{Li}_2\text{O-SiO}_2$ glasses in Britton-Robinson universal buffers

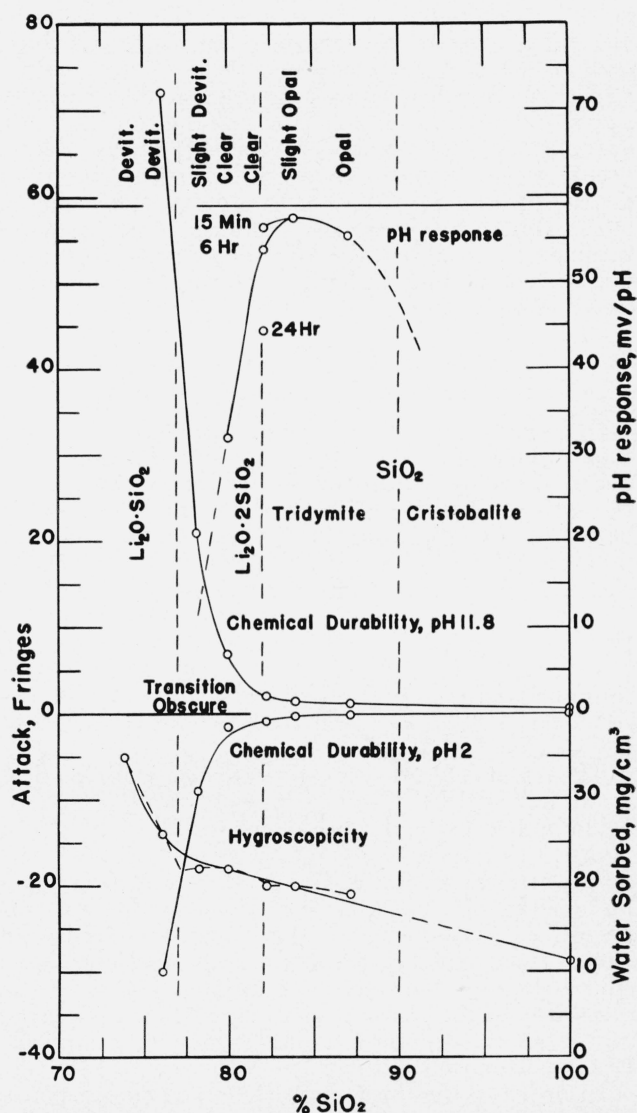
Glasses ^a		Chemical durability (6 hr, 80° C) at pH						pH response, 4.1 to 8.2 after soaking			Working characteristics
Li_2O	SiO_2	2.0	4.1	6.0	8.2	10.2	11.8	15 min	6 hr	24 hr	
%	%	<i>Fringes</i>	<i>Fringes</i>	<i>Fringes</i>	<i>Fringes</i>	<i>Fringes</i>	<i>Fringes</i>	<i>mv/pH</i>	<i>mv/pH</i>	<i>mv/pH</i>	Devitrified. Slight devitrification. Clear. Do. Slight opal. Opal.
23.9	76.1	30 swell	30 swell	30 swell	24 swell	30 attack	72 attack	(e)	-----	-----	
21.8	78.2	9 swell	9 swell	9 swell	9 swell	6 attack	21 attack	(e)	-----	-----	
20.0	80.0	1½ swell	1½ swell	1½ swell	2- swell	1½ attack	7 attack	32.5	-----	14.0	
17.8	82.2	1- swell	1- swell	½+ swell	½+ swell	SC ^d	2 attack	56.5	54.0	44.5	
16.1	83.9	¼ swell	¼ swell	¼ swell	¼ swell	SC ^d	1½ attack	57.5	57.5	57.5	
12.9	87.1	½+ swell	½+ swell	½+ swell	D ^e swell	SC ^d	1+ attack	-----	55.5	55.5	
Fused SiO_2		ND ^b	ND ^b	ND ^b	ND ^b	ND ^b	½ attack	(f)	(f)	(f)	

^a Series B of table 1.^b ND, not detectable.^c D, detectable.^d SC, surface cut.^e Devitrified.^f No definite pH response.FIGURE 3. Chemical durability of $\text{Li}_2\text{O-SiO}_2$ glasses.

Britton-Robinson universal buffer mixtures, 6 hours, 80° C.

4. Relation Between pH Response, Hygroscopicity, and Chemical Durability

An over-all picture of the dependence of pH response of the $\text{Li}_2\text{O-SiO}_2$ glasses on their chemical durability and hygroscopicity is shown in figure 4. The pronounced decline in the chemical durability for members of this series having increased Li_2O

FIGURE 4. Comparison of the pH response, the hygroscopicity, and the chemical durability at pH 2 and 11.8 of a series of $\text{Li}_2\text{O-SiO}_2$ glasses.

The approximate compositions at which a new primary phase appears in the equilibrium diagram are indicated by vertical lines. Hygroscopicity values (1-hr exposure) are for glasses "B" table 1, except for 73.5 percent SiO_2 —two possible curves are drawn through the resulting composite data.

content, as indicated by the curves for attack and swelling at pH 11.8 and pH 2, respectively, is associated with an equally pronounced failure in the pH response of electrodes prepared from these glasses. Although the composition range over which successful electrodes can be prepared is restricted by the appearance of coarse devitrification for the glasses of lower percentages of SiO_2 upon reheating for the purpose of blowing the electrode bulbs, and by the appearance of opals in the higher SiO_2 members, the pH response-composition curve obviously indicates an optimum similar to those found for all other series of glasses previously investigated [11, 12, 13].

The correspondence between the departures of the pH response-composition curve and some of the critical compositions of the phase equilibrium diagram is rather striking, with the optimum performance appearing in the composition range in which tridymite is the primary phase [19].

Perhaps the most interesting and possibly the most significant feature of these data is the fact that the optimum pH response for the $\text{Li}_2\text{O-SiO}_2$ glasses occurs at much lower values of hygroscopicity than do the optima for $\text{Na}_2\text{O-SiO}_2$ and $\text{K}_2\text{O-SiO}_2$ glasses [13]. Whether this has any significant bearing on an ultimate acceptable theory for the glass electrode can only be ascertained in light of much additional data on other series of glasses.

5. Comparison of pD Response and pH Response of $\text{Li}_2\text{O-SiO}_2$ Glasses

In an effort to obtain some information concerning the response of silicate glasses to deuterium ions, the difference in potential for electrodes prepared from the glasses of the $\text{Li}_2\text{O-SiO}_2$ series was determined between two solutions of limited buffer capacity prepared from D_2O by the use of P_2O_5 and CaO .⁵ These materials were chosen because they did not introduce hydrogen ions, and at the same time they produced buffers, from inexpensive compounds, having a wide pD interval. The apparent values (obtained with a calibrated glass electrode) of the resulting buffers were pD 0.65 for the D_3PO_4 and pD 12.4 for Ca(OD)_2 .

The results obtained for pD response and chemical durability of the $\text{Li}_2\text{O-SiO}_2$ glasses in these deuterium oxide buffers are given in table 4 and plotted (○) in figure 5. A comparison of these results with the data obtained with the Britton-Robinson universal buffers (fig. 4) indicates that the response to deuterium ions is superior to the response to hydrogen ions. However, a glance at the respective durability curves reveals that there is a marked superiority in durability of the glasses, especially at high alkalinity, in the special deuterium buffers over the aqueous Britton-Robinson buffers.

In order to obtain a more rigorous comparison, a set of parallel experiments were performed using water buffers prepared with the same constituents and of equal concentration as the deuterium oxide

⁵ The deuterium oxide having a certified purity of 99.8 percent of D_2O was obtained from stock available in the Bureau's Mineral Products Division, originally purchased from the Sturatt Oxygen Co. of San Francisco, Calif., by permission of the Atomic Energy Commission.

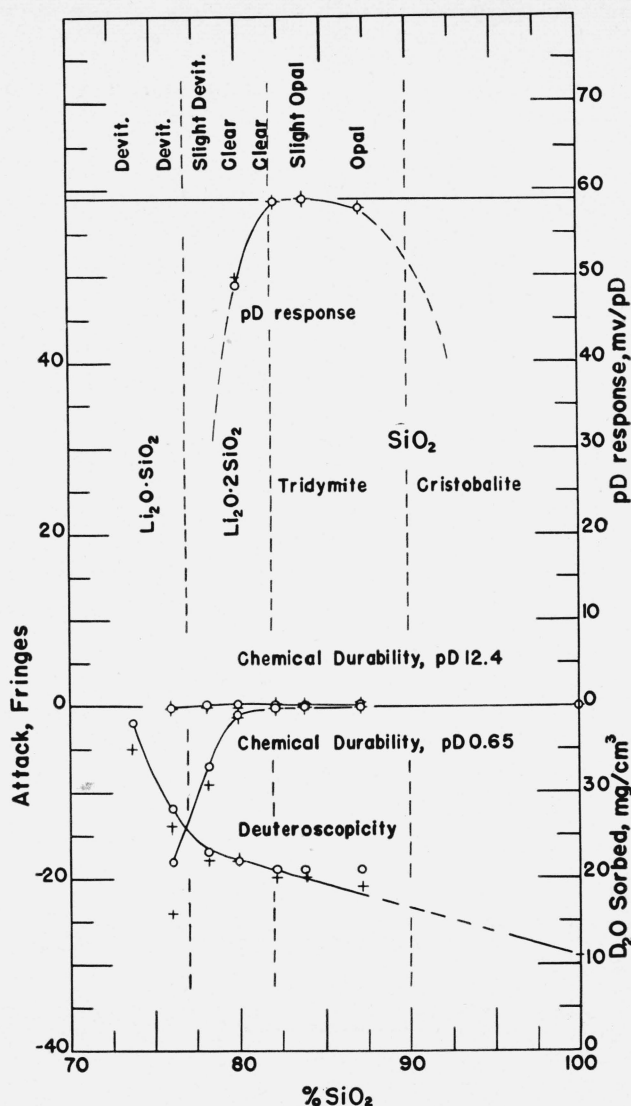


FIGURE 5. Performance of $\text{Li}_2\text{O-SiO}_2$ glasses in D_2O solutions compared with the performance in H_2O solutions.

(○), the pD response and chemical durability in deuterium oxide solutions of— D_3PO_4 , pD 0.65; and saturated Ca(OD)_2 , pD 12.4 (+), the pH response and chemical durability in aqueous solutions of H_3PO_4 , pH 0.65 and saturated Ca(OH)_2 , pH 12.3.

solutions (Data listed in table 4 and plotted (+) in fig. 5.). When this was done, no significant differences in pH and pD response were detected. However, the impression remained that the electrode performances were slightly steadier in the deuterium oxide than in the aqueous solutions. In accordance with this, the amount of swelling observed in the acid deuterium oxide was less than in the corresponding aqueous solutions. It is also interesting to note that three of the glasses showed swelling in the saturated solution of Ca(OH)_2 above pH 12, while only one of them did so in the saturated solution of Ca(OD)_2 . It should also be pointed out that the saturated solution of Ca(OD)_2 had an apparent pD approximately 0.1 of a unit higher than the pH of the Ca(OH)_2 .

TABLE 4. pH and pD response, hygroscopicity, and deuterioscopicity, chemical durability in aqueous and deuterium oxide buffers prepared from P_2O_5 and CaO, of a series of Li_2O - SiO_2 glasses

Glasses (B) table 1, except for glass containing 73.87 percent of SiO_2									
Glasses		Vapor sorbed 1 hr		Electrode response between—		Chemical durability (attack)			
Li_2O	SiO_2	H_2O	D_2O	pH 0.65 and 12.3	pD 0.65 and 12.4	H_3PO_4 pH 0.65	D_3PO_4 Apparent pD 0.65	$Ca(OH)_2$ pH 12.3	$Ca(OD)_2$ Apparent pD 12.4
%	%	mg/cm ³	mg/cm ³	mV/pH	mV/pD	Fringes	Fringes	Fringes	Fringes
26.13	73.87	35	38	(a)	-----	24 swell-----	18 swell-----	1/4 swell, pitted..	1/10 swell.
23.9	76.1	26	28	(a)	-----	9 swell-----	7 swell-----	Swell, pitted..	1/4 attack.
21.8	78.2	22	23	(b)	-----	1+ swell-----	1 swell-----	1/4 swell, pitted..	1/4- attack.
20	80	22	22	50	49	1/4 swell-----	1/4- swell-----	2/10 attack-----	2/10 attack.
17.8	82.2	20	21	58.7	58.7	2/10- swell-----	1/10 swell-----	1/10 attack-----	1/10 attack.
16.1	83.9	20	21	59	59	D ^d swell-----	D ^d swell-----	1/10 attack-----	1/10- attack.
12.9	87.1	19	21	58	58				
Fused SiO_2 ---		11	-----	(c)	(c)	ND ^e swell-----	ND ^e swell-----	2/10 attack-----	1/10+ attack.
Corning 015---		104	111	58.4	58.1	2/10 swell-----	D ^d swell-----	1/4- attack-----	2/10 attack.

^a Devitrified while blowing electrodes. ^b Slight devitrification. ^c No definite electrode response. ^d D, detectable. ^e ND, not detectable.

6. Lithium Ion Response of Electrodes Prepared From Li_2O - SiO_2 Glasses

The question is often raised concerning the equilibrative response of glass electrodes to positive ions other than hydrogen, especially to ions common to both the solution and to the glass. In the present case the response to lithium ions of an electrode prepared from the lithium silicate glass (Li_2O , 12.9%; SiO_2 , 87.1%) was determined over the range pLi 1 to 3 in solutions containing $LiNO_3$ to which 1 ml of glacial acetic acid per 50 ml of solution was added to maintain a constant pH during the observations. If one assumes that all of the voltage change observed between the glass electrode and the saturated calomel reference cell over this pLi range can be attributed to the response of the glass electrode to Li^+ ions, the pLi response of the Li_2O - SiO_2 glass was less than 1 mV per pLi. For all practical purposes it can be stated that a pLi response of electrodes prepared from this Li_2O - SiO_2 glass is essentially absent, whereas a full pH and pD response is present.

It would be interesting to extend these investigations to a study of the response of the glass electrode to tritium ions.

7. Summary

The pH and pD response of electrodes prepared from a series of Li_2O - SiO_2 glasses have been compared with the hygroscopicity, deuterioscopicity, and chemical durability of the glasses in aqueous and deuterium oxide buffers. The curves for pH and pD response as a function of composition passed through an optimum electrode response that was limited on the low-silica end by poor chemical durability and a strong tendency toward devitrification of the glasses while the electrodes were being blown. The optimum also fell off on the high-silica end where opalescence appeared and the hygroscopicities and deuterioscopicities decreased. The optimum electrode performance was attained by those glasses that most nearly approximated the properties of

Corning 015. However, this optimum appeared at lower sorption values than were found for Corning 015 and other glass systems previously investigated.

Electrodes prepared from the Li_2O - SiO_2 glasses apparently respond to deuterium ions as readily as to hydrogen ions.

In the present experiments the Li_2O - SiO_2 glasses showed detectably more swelling in the acid aqueous than in the acid deuterium oxide solutions. Interesting examples of swelling in alkaline buffers above pH and pD values of 12 were observed. The apparent pD values for saturated $Ca(OD)_2$ were slightly higher than for the corresponding $Ca(OH)_2$ buffer.

The pH and pD response, hygroscopicity, and deuterioscopicity, as well as the chemical durabilities in aqueous and deuterium oxide solutions, appear to reflect some of the critical features of the Li_2O - SiO_2 phase-equilibrium diagram with the optimum electrode response occurring in the composition range in which tridymite is the primary phase.

8. References

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